APPENDIX F

Monitored Natural Attenuation Summary

Source: IT, 1999 (Chapter 5.0)

302841 3020 286

PETROLEUM, OIL, and LUBRICANT OUTPARCEL
CLOSURE REPORT
BRAC PROPERTY
HAMILTON ARMY AIRFIELD
NOVATO, CALIFORNIA

CONTRACT NO. DACW05-95-D-0001 DELIVERY ORDER NUMBER 0006

Submitted to:

U.S. Army Corps of Engineers
Sacramento District
1325 J Street
Sacramento, California 95814-2922

Submitted by:

IT Corporation 4005 Port Chicago Highway Concord, California 94520

Revision C

December 23, 1999

	Issued to:	<u>. </u>	Date:
--	------------	--	-------

5.0 Natural Attenuation Summary

In conjunction with the March/April 1998 and September/October 1998 groundwater monitoring events, groundwater samples were collected and analyzed for hydrogeologic chemical indicators of biodegradation of petroleum hydrocarbons. This section provides the evidence that natural attenuation is occurring at the POL Outparcel, including

- A petroleum-hydrocarbon (i.e., TPH) plume is evident under the former location of AST-2. The plume orientation tends to conform with groundwater flow patterns. However, the plume is not migrating and is shrinking.
- Trend shows either a static or diminishing petroleum-hydrocarbon groundwater plume.
- Benzene, toluene, ethylbenzene, and xylene do not appear to be present in most of the wells, and where present, have diminished over time.
- Geochemical indicators of natural attenuation are present.

These lines of evidence are defined in ASTM Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites (1998) and are necessary for demonstrating the appropriateness of remediation by natural attenuation. The primary line of evidence is generally considered enough to demonstrate natural attenuation at the site is a viable remedial alternative, but secondary lines of evidence are required when the monitoring data are limited or are not conclusive.

This section is organized into four subsections. Section 5.1 describes the operative mechanisms of contaminant attenuation and geochemical indicators that demonstrate natural attenuation is occurring. Sections 5.2 and 5.3 discuss historical TPH concentrations and the results of two rounds of monitoring for geochemical indicators of natural attenuation at the site. Section 5.4 summarizes the primary and secondary lines of evidence that natural attenuation is occurring at the POL Outparcel.

5.1 Operative Mechanisms and Geochemical Indicators of Natural Attenuation
Natural attenuation is the reduction in concentration and mass of a contaminant plume due to
processes occurring naturally in the environment. Natural attenuation occurs through a
combination of physical, chemical, and biological processes, including volatilization, dispersion,

dilution, sorption, and biodegradation (also known as intrinsic bioremediation). All of these processes contribute to a measurable reduction of the concentrations of contaminants within the plume. Biodegradation, however, is the only process that can produce significant reduction of the total mass of the contaminant plume via conversion of the hydrocarbons into carbon dioxide and water (Buscheck et al., 1996).

Hydrocarbon biodegradation is a series of microbially mediated chemical reactions that produce changes in the ambient geochemistry of the groundwater in which the reactions occur (AFCEE, 1995). The occurrence of biodegradation is indicated by measured trends in several geochemical parameters. In general, any of the following trends observed across a dissolved TPH plume (with increasing contaminant concentration) would suggest the occurrence of natural biodegradation:

A relative decrease in: dissolved oxygen oxidation-reduction potential (redox) nitrate sulfate A relative increase in: ferrous iron alkalinity methane sulfide

Dissolved oxygen (D.O.) is the most thermodynamically favored electron acceptor used in the biodegradation of petroleum hydrocarbons (AFCEE, 1995). Aerobic biodegradation decreases the available D.O. in the groundwater and provides one of the best indicators of fuel biodegradation. However, it is difficult to collect representative readings when monitoring wells do not recharge adequately during purging and sampling. Excessive drawdown (greater than 5 percent of the standing water in the well) during the purge cycle tends to aerate the well water and inflate the D.O. readings above ambient levels. The POL Outparcel wells are screened in relatively low permeability bedrock and aeration of the well water during purging is a problem with many of the wells.

Oxidation-reduction (redox) potential of groundwater is a measure of the electron activity and indicates the relative tendency of a solution to accept or transfer electrons (AFCEE, 1995). Redox reactions in petroleum-hydrocarbon-contaminated groundwater are usually biologically mediated; therefore, the redox potential of a groundwater system depends upon and influences rates of biodegradation. Redox potentials within the plume are lower than those outside the plume and are often correlative with dissolved oxygen concentrations. The areas where oxygen has been depleted by biodegradation tend to have the lowest redox potentials.

After the D.O. is depleted by biodegradation, nitrate, iron, and sulfate may be used as electron acceptors for anaerobic biodegradation. Utilization of nitrate during biodegradation can produce a marked decrease of nitrate in wells screened within the hydrocarbon plume. Utilization of ferric iron and sulfate for anaerobic degradation produces ferrous iron and sulfide, respectively. An increase in these parameters (above background concentrations) within the plume provides another indicator of biodegradation.

Methanogenesis is another biodegradation process that can occur under anaerobic conditions. This process generally occurs after oxygen, nitrate, iron, and sulfate have been depleted by biodegradation (AFCEE, 1995). During methanogenesis, carbon dioxide is used as an electron acceptor and methane is produced. The presence of methane in groundwater within the plume provides an indication of microbial degradation when concentrations exceed background.

Alkalinity variations across the hydrocarbon plume can also provide evidence of biodegradation. Alkalinity tends to be higher in wells located within the hydrocarbon plume than those positioned outside the plume.

Other parameters that provide useful information about biodegradation include pH and temperature. These parameters do not provide direct evidence that biodegradation is occurring, but indicate if the physical and chemical conditions of the groundwater system are conducive to biodegradation. For example, biodegradation operates best when the pH is between six and eight and at temperatures between 16 and 20 degrees Celsius (°C) (Buscheck and O'Reilly, 1995).

5.2 Historical Total Petroleum Hydrocarbon/Benzene, Toluene, Ethylbenzene, and Xylene Concentrations

Groundwater monitoring data have been collected at the POL Outparcel since 1992, but the monitoring frequency and analytical procedures have varied, creating some difficulties in evaluating temporal and spatial plume trends. Monitoring was sporadic from 1992 to 1996 as only three events were conducted. Since February 1997, most of the POL Outparcel wells have been sampled five or six times. During the initial two monitoring events conducted between July and September 1992, TPH was quantified using EPA Method 418.1 (EPA, 1995). This method is nonspecific and does not accurately quantify petroleum hydrocarbons in the volatile range. In subsequent monitoring events, TPH was quantified using the more accurate EPA Method 8015M. The TPH results from 1992; therefore, are not comparable to later TPH results and the EPA Method 418.1 results have been omitted from discussion of TPH trends below.

Total petroleum hydrocarbon concentrations have decreased since groundwater monitoring was implemented in 1992. Table 4-1 summarizes the TPH and BTEX concentrations for wells PL-MW-101, -103, -104, -114, and -115 and MW-POLA-121 located in or immediately downgradient of the source area (AST-2). Total petroleum hydrocarbon concentrations have decreased in all of these wells except PL-MW-101, where concentrations have fluctuated between 3,900 to 11,600 μg/L. Concentrations of TPH in wells PL-MW-103, -114, and -115 and MW-POLA-121 have actually decreased to just above or below 50 μg/L, the method detection limit for TPH.

Initial concentrations of BTEX detected in wells PL-MW-101 and MW-POLA-121 (Table 5-1) have declined significantly since 1992. Benzene and toluene were detected in PL-MW-101 in 1992, but have not been detected in subsequent events. Ethylbenzene and total xylenes in well PL-MW-101 have decreased from initial concentrations of 110 and 290 µg/L in July 1992 to 39 and 47 µg/L in October 1998, respectively. Benzene, ethylbenzene, and total xylenes were detected in well MW-POLA-121 during the February and March 1997 monitoring events, but these hydrocarbons were not detected during the subsequent monitoring events. Benzene, toluene, ethylbenzene, and xylenes have not been detected in wells PL-MW-103, -104, -114, and -115 during any monitoring events.

Total petroleum hydrocarbon isoconcentration contours for the March 1994, February 1997, March/April 1998, and January 1999 monitoring events show that the plume is shrinking (see Figure 4-1). The isoconcentration contours for 100 and 500 µg/L have clearly receded toward the source area since 1994, and the areal extent of the plume has been reduced by approximately 50 percent. The portion of the plume containing TPH concentrations in excess of the GSA Phase I Sale Area RCG of 1,200 µg/L also appears to be shrinking.

5.3 Geochemical Indicators

The geochemical parameters collected during the March/April 1998 and September/October 1998 monitoring events provide additional evidence for biodegradation of the TPH plume (Tables 5-1 and 5-2). Of the parameters, D.O., redox potential, ferrous iron, and methane data follow the expected trends described in Section 5.1 for evidence of biodegradation. Isoconcentration maps of these parameters are provided in Figures 5-1 through 5-8.

The data are contoured for wells PL-MW-101, -103, -104, -114, -115, and -116 and MW-POLA-120 and -121 only because these wells are located within and just outside the petroleum-hydrocarbon groundwater plume.

The geochemical parameters show the following conditions and lateral trends that are indicative of TPH biodegradation (Tables 5-1 and 5-2):

- Dissolved oxygen concentrations are lowest at wells PL-MW-101 and -104 and MW-POLA-121, these are the closest to the former AST-2. Dissolved oxygen concentrations in these wells ranged from 0.5 to 0.6 milligrams per liter (mg/L) and 0.8 to 1.94 mg/L during the March/April 1998 and September/October 1998 monitoring events, respectively. Also, these wells have the highest hydrocarbon concentrations, i.e., low D.O. coincides with high concentration portion of the hydrocarbon plume. The September/October 1998 D.O. concentrations were probably lower than actually measured, but some aeration occurred due to excessive drawdown during well purging. Dissolved oxygen concentrations generally increase with distance from these wells and the source area. This pattern provides a strong indication that aerobic biodegradation of the hydrocarbons has occurred.
- Redox potentials are lowest at PL-MW-101, MW-POLA-121, and PL-MW-104, ranging from -255.6 to 11.5 millivolts (mV). The lowest redox potentials (-255.6 and -228.8 mV) were measured in well PL-MW-101, which also had the highest concentrations of TPH and lowest D.O. concentrations. Except for well PL-MW-115, which had a redox potential of 11 mV during the September/October 1998 monitoring event, all other wells had higher redox potentials in March/April 1998. These data indicate that conditions have become reducing (through oxygen depletion) in the area of highest TPH concentrations, and support the conclusion drawn from the D.O. concentrations that aerobic biodegradation of the hydrocarbons has occurred.
- Ferrous iron concentrations were highest in wells nearest the former AST, which is consistent with the results for D.O. and redox. Ferrous iron concentrations were much higher during the September/October 1998 monitoring event, with a maximum concentration of 2.88 mg/L detected in well MW-POLA-121.
- Methane concentrations were consistently highest in wells PL-MW-101, -104, and -115 and MW-POLA-121, 0.04 to 2.8 mg/L and 0.05 to 3.2 mg/L, respectively. This indicates that methanogenesis has occurred in the center of the hydrocarbon plume.
- The pH of all samples ranged from roughly six to eight, the range most favorable for TPH biodegradation.

- The temperature of the groundwater samples ranged from 16 to 20°C during the March/April 1998 monitoring event and 20 to 27°C during the September/October 1998 monitoring event. These differences in temperature probably reflect normal seasonal variation. The lower temperature range measured in March/April 1998 is more favorable for biodegradation of fuels because oxygen is more soluble in cold water.
- Nitrate may not be a suitable electron acceptor at this site because it was not detected in wells near the former AST, and the maximum concentration in wells outside the plume was only 1.3 mg/L. It is possible that the available nitrate was consumed by biodegradation of the TPH plume, but the low concentrations detected in wells outside the plume suggest that it is not an important electron acceptor for the POL Outparcel.
- The total alkalinity (expressed as CaCO₃) data are not conclusive, as concentrations within the plume are comparable to those outside the plume. In general, areas contaminated by fuel hydrocarbons may exhibit a total alkalinity that is higher than that seen in background areas. However, a trend may never be evident since naturally occurring calcite in the Franciscan bedrock would affect the alkalinity of the pore water. This is because the microbially-mediated reactions causing biodegredation can yield an increase in the total alkalinity of the system. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction, and less pronounced during methanogenesis.
- The sulfate and sulfide data are not conclusive. After dissolved oxygen, nitrate, and bioavailable iron have been depleted in the microbial treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegredation. This process is termed sulfate reduction and results in the production of sulfide. Sulfate concentrations are used as an indicator of anaerobic degradation of fuel compounds. Therefore, the expected trend is decreasing sulfate and increasing sulfide toward the center of the plume. In general, sulfate concentrations are lower in wells nearest the former AST-2, but sulfide was not detected in any wells during the March/April 1998 monitoring event. However, if the dissolved oxygen, nitrate, and bioavailable iron have not been depleted, sulfate may not have yet been reduced, and therefore, sulfides may have not been produced. A maximum sulfide concentration of 0.36 mg/L was detected in the source area well, well PL-MW-101 during the September/October 1998 monitoring event, but sulfide was also detected in many wells outside the plume. However, sulfide detections in the wells outside the plume may be influenced by the chemical composition of the Bay Mud (where some of the wells are screened) compared to the result of microbial reactions.

The data collected on these parameters (especially D.O. and redox potential) strongly indicate that intrinsic bioremediation has occurred at the POL Outparcel. The data show the typical progression from aerobic to anaerobic biodegradation as oxygen is depleted in the area of highest TPH concentrations.

5.4 Summary

The groundwater monitoring data collected at the POL Outparcel indicate the TPH plume is shrinking and natural attenuation is occurring. The lines of evidence for natural attenuation include the following:

- With the exception of well PL-MW-101 that is located near the center of the source area, TPH concentrations have declined significantly since March 1994. The areal extent of the TPH plume was reduced by approximately 50 percent since March 1994.
- Concentrations of TPH in well PL-MW-101 does appear to be relatively stable, i.e., not increasing (see Table 4-1).
- Concentrations of BTEX constituents have declined in all wells since 1992, including well PL-MW-101. Except for well PL-MW-101, BTEX was not detected in any other wells since March 1997.
- Geochemical indicators (i.e., D.O., redox potential, ferrous iron, methane, and sulfate) follow the expected trends for a TPH plume undergoing biodegradation.

These data trends indicate natural attenuation, with groundwater monitoring as a viable remedial action for the POL Outparcel.

Table 5-1. Geochemical Indicators March/April 1998 Monitoring Event

. Well	Dissolved Oxygen (mg/L)*	Redox (millivolts)	Ferrous Iron (mg/L)	Methane (mg/L)	Sulfate (mg/L)	Total Sulfide (mg/L)	Nitrate (mg/L)	Total Alkalinity as CaCO ₃ (mg/L)	рН	Temperature (°C)b
PL-MW-101	0.50	-225.6	0.07	2.8	53	ND (<0.05)°	ND (<0.05)	516	6.96	19.4
PL-MW-103	0.70	121.1	ND (<0.05)	0.0039	69	ND (<0.05)	0.24	205	6.87	16.8
PL-MW-104	0.60	24.6	0.01	0.04	10 [:]	ND (<0.05)	ND	509	6.78	18.7
PI-MW-105	6.40	217.1	0.01	ND (<0.002)	- 56	ND (<0.05)	0.45	239	7.47	19.2
PL-MW-106	5.20	217.7	ND (<0.05)	0.0028	105	ND (<0.05)	0.09	493	7.30	16.6
PL-MW-107	6.50	174.0	0.01	ND (<0.002)	261	ND (<0.05)	0.10	749	8.05	19.7
PL-MW-108	3.30	221.1	NS⁴	ND (<0.002)	31	ND (<0.05)	ND (<0.05)	248	7.43	18.9
PL-MW-109	5.50	214.0	NS	0.0056	48	ND (<0.05)	ND (<0.05)	413	7.03	19.0
PL-MW-111A°	5.70	197.3	ND (<0.05)	ND (<0.002)/ND (<0.002)	249/252	ND (<0.05)	ND (<0.05)/ND (<0.05)	369/368	7.12	12.6
PL-MW-111B	5.00	224.7	ND (<0.05)	ND (<0.002)	234	ND (<0.05)	ND (<0.05)	388	7.32	20.0
PL-MW-112A ^e	2.80	217.3	ND (<0.05)	ND (<0.002)	357	ND (<0.05)	0.10	445	7.55	16.3
PL-MW-112B	4.20	146.5	ND (<0.05)	ND (<0.002)	175	ND (<0.05)	0.19	403	7.99	20.2
PL-MW-113A°	2.60	114.0	0.01	0.0022	6360	ND (<0.05)	ND (<0.05)	654	6.90	16.5
PL-MW-113C	2.90	187.4	ND (<0.05)	0.0096	277	ND (<0.05)	ND (<0.05)	596	7.65	17.7
PL-MW-114	1.40	179.0	0.01	ND (<0.002)	49	ND (<0.05)	0.06	176	7.40	17.7
PL-MW-115	1.00	144.5	0.02	0.058/0.062	132/130	ND (<0.05)	ND (<0.05)/ND (<0.05)	300/301	7.35	17.0
PL-MW-116	6.70	197.4	ND (<0.05)	ND (<0.002)	26	ND (<0.05)	1.3	165	6.94	17.3
PL-MW-117A°	2.60	190.7	0.01	ND (<0.002)	137	ND (<0.05)	0.27	320	7.50	16.1
PL-MW-117B	3.60	137:4	ND (<0.05)	ND (<0.002)/ND (<0.002)	125/122.	ND (<0.05)	0.50/0.49	275/277	8.12	19.9
MW-POLA-118	3.20	184.1	ND (<0.05)	ND (<0.002)	173	ND (<0.05)	0.90	273	7.30	17.1
MW-POLA-119	1.90	146.9	0.01	ND (<0.002)	191	ND (<0.05)	0.22	337	7.12	20.6
MW-POLA-120	2.60	203.7	0.02	ND (<0.002)	119	ND (<0.05)	0.62	242	7.11	19.9
MW-POLA-121	0.60	11.5	ND (<0.05)	0.12	15	ND (<0.05)	ND (<0.05)	128	6.42	17.9

^a Milligrams per liter

Checked by MMS 13-33-49
Approved by A w S (2-25-78

^b Degrees Celsius

c Not detected above practical quantitation limit (practical quantitation limit is in parenthesis)

d Not sampled

^{*} These are nested well pairs which are completed with a shallow zone (A) and deep zone (B)

¹ Original sample result/field duplicate result

Table 5-2. Geochemical Indicators September/October 1998 Monitoring Event

Well	Dissolved Oxygen (mg/L) ^a	Redox (millivolts)	Ferrous Iron (mg/L)	Methane (mg/L)	Sulfate (mg/L)	Total Sulfide (mg/L)	Nitrate (mg/L)	Total Alkalinity as CaCO ₃ (mg/L)	рН	Temperature (°C) ^b
PL-MW-101	0.82	-228.8	0.22	3.2	53	0.36	ND (<0.05) ^c	544	6.94	21.23
PL-MW-103	2.85	79.9	0.29	0.010	109	0.01	ND (<0.05)	240	6.94	22.24
PL-MW-104	1.94	-50.2	0.01	0.15	8 :	ND (<0.05)	ND (<0.05)	556	6.77	25.38
PI-MW-105	5.59	350.2	ND (<0.05)	ND (<0.002)	58	0.01	ND (<0.05)	242	7.25	23.15
PL-MW-106	2.12	131.3	ND (<0.05)	0.0046	107	0.03	0.088	514	7.24	25.49
PL-MW-107	7.99	285.2	ND (<0.05)	ND (<0.002)	210	0.12	0.06	756	8.12	22.49
PL-MW-108	4.31	254.7	0.05	ND (<0.002)	64	0.04	0.065	462	7.18	24.07
PL-MW-109	5.45	215.8	0.03	ND (<0.002)	51	0.02	ND (<0.05)	429	7.04	25.42
PL-MW-111Ad	1.00	145.1	0.02	ND (<0.002)/ND (<0.002) ^e	270/261	0.05	ND (<0.05)/ND (<0.05	389/391	6.91	25.91
PL-MW-111B	1.05	172.4	0.01	ND (<0.002)	250	ND (<0.05)	ND (<0.05)	397	6.93	25.76
PL-MW-112Ad	2.90	205.4	0.01	ND (<0.002)	571	0.13	0.13	562	7.14	22.46
PL-MW-112B	1.35	190.8	ND (<0.05)	ND (<0.002)	202	0.01	0.18	416	7.50	21.02
PL-MW-113A ^d	3.60	204.5	0.01	ND (<0.002)	7360	0.01	ND (<0.05)	688	6.80	25.92
PL-MW-113C	2.13	184.0	ND (<0.05)	0.0059	282	0.01	ND (<0.05)	614	7.55	23.29
PL-MW-114	1.52	225.6	ND (<0.05)	0.13	78	ND (<0.05)	0.055	227	7.06	20.73
PL-MW-115	2.10	10.6	ND (<0.05)	0.052/0.051	137/148	0.01	ND (<0.05)/ND (<0.05	281/283	7.09	21.16
PL-MW-116	6.11	285.5	0.01	ND (<0.002)	29	0.04	0.98	166	6.96	22.24
PL-MW-117A	3.61	231.2	ND (<0.05)	ND (<0.002)	143	0.05	0.42	322	7.57	25.71
PL-MW-117B	2.00	242.3	ND (<0.05)	ND (<0.002)/ND (<0.002)	125/125	0.01	0.54/0.55	264/264	7.89	25.47
MW-POLA-118	1.50	186.2	0.81	ND (<0.002)	219	0.26	1	303	7.04	27.80
MW-POLA-119	2.11	144.1	0.08	ND (<0.002)	196	0.02	0.35	315	7.18	25.60
MW-POLA-120	2.82	183.3	ND (<0.05)	ND (<0.002)	114	ND (<0.05)	0.9	231	7.05	20.74
MW-POLA-121	1.91	-61.5	2.88	0.6	13	0.06	ND (<0.05)	404	6.81	22.77

^a Milligrams per liter

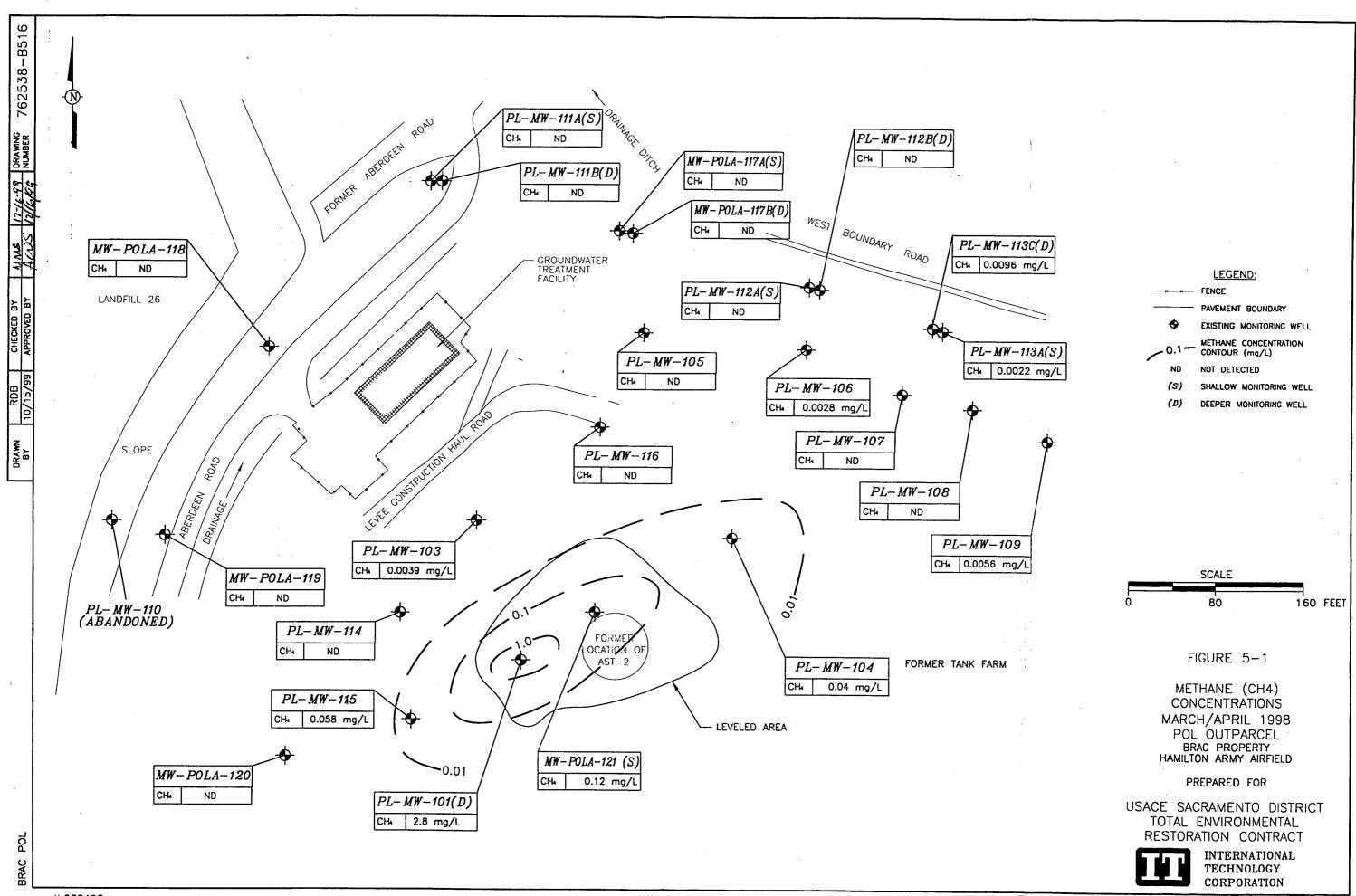
Checked by <u>MMS/223-99</u>
Approved by <u>AUS 12-23</u>-19

Degrees Celcius

^c Not detected above practical quantitation limit (practical quantitation limit is in parenthesis)

^d These are nested well pairs which are completed within a shallow zone (A) and deep zone (B)

^e Original sample/duplicate sample



meth030498

